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Characterization of Carbide Lime to Identify Sulfite Oxidation Inhibitors

Radian Corp, Austin, TX

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

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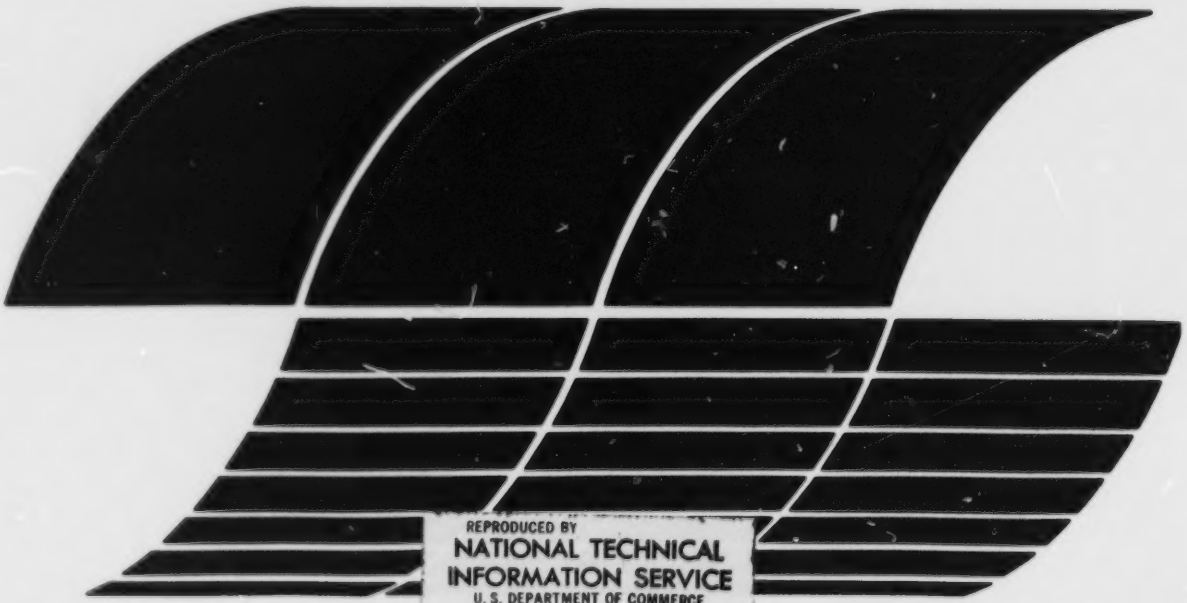

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16. ABSTRACT The report gives results of a study of carbide lime--a by-product of acetylene manufacture, primarily calcium hydroxide--used in a flue gas desulfurization (FGD) system at Louisville Gas and Electric (LGE). The study was undertaken to: identify sulfite ion oxidation inhibitors in carbide lime, and develop an analytical method for sulfite that avoids the interferences observed in analyzing scrubber liquors from LGE's FGD system. Thiosulfate was identified as the oxidation inhibitor in carbide lime; it was also identified (along with other reduced sulfur species) as a source of interference in the iodine titration method used at LGE for sulfite analysis. Bench-scale tests verified the presence of thiosulfate as a major inhibition to sulfite oxidation in simulated scrubber liquors. This means that the low oxidation rate (e.g., that reported at LGE with carbide lime) results in a greatly reduced tendency to calcium sulfate (gypsum) scaling, therefore a greatly improved FGD system reliability. The amount of thiosulfate required for scale-free scrubber operation is unknown. However, to bring the thiosulfate level of commercial lime up to that found in carbide lime would cost $1.50 per ton of lime (using sodium thiosulfate pentahydrate at $12 per 100 pounds). The ion chromatograph was found to be the best analytical tool for determining sulfite concentrations in carbide lime liquors.

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Properties	Iodine	Carbide Lime	14B	
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1.0 INTRODUCTION

Recent testing under EPA sponsorship at Louisville Gas and Electric's (LG&E) Paddy's Run flue gas desulfurization (FGD) unit has shown a significant difference between carbide lime, a byproduct of acetylene manufacture, and commercial lime. The most significant difference was the extremely low rate of oxidation of sulfite to sulfate when carbide lime was used. The low oxidation rate results in a greatly reduced tendency for calcium sulfate (gypsum) scaling. Also, a significant interference with Radian's liquid sulfite analytical technique (iodometric titration in a pH 6 buffer) was apparent when carbide lime was being used.

The main component of carbide lime is hydrated calcium oxide, $Ca(OH)_2$, but it also contains numerous impurities. Carbide lime is made under generally reducing conditions and thus many of the contained impurities are in reduced oxidation states.

This study was undertaken to characterize carbide lime, identify the possible sulfite oxidation inhibitors and evaluate methods for sulfite and sulfate analysis in carbide lime liquors. The characterization of carbide lime involved various instrumental and wet chemical techniques to identify the major and minor species in carbide lime. These species were then evaluated as possible oxidation inhibitors. Candidates for sulfite oxidation inhibitors were tested in the laboratory. Finally, interference-free methods for sulfite and sulfate analysis were evaluated.

2.0 SUMMARY AND CONCLUSIONS

Carbide lime was characterized using several analytical techniques. A survey analysis for elemental composition was done by spark source mass spectrometry. The organic compounds in carbide lime were determined on a gas chromatograph-mass spectrometer. And the sulfur species present were analyzed by both wet chemical and instrumental methods. The physical characteristics of carbide lime were determined by X-ray powder diffraction and infrared spectrophotometry.

Laboratory tests were conducted to compare the rate of sulfite-to-sulfate oxidation in the presence of:

- carbide lime,
- commercial lime and
- oxidation inhibitors found in carbide lime.

Several methods were tested for analyzing sulfite and sulfate in carbide lime liquors. Radian normally uses an iodometric titration in a pH 6 buffer to determine sulfite concentrations. However, in carbide lime liquors a species other than sulfite reacts to consume the iodine, resulting in a high apparent sulfite concentration. There is no interference with normal sulfate analysis in carbide lime, but the sulfite present must be prevented from oxidizing to sulfate.

From the results of this work, it can be concluded that sulfur species in reduced oxidation states in carbide lime cause both the inhibited sulfite oxidation and the interference with the sulfite analysis.

The characterization studies showed that most of the sulfur in carbide lime was present in a reduced oxidation state. One reduced sulfur species, thiosulfate, was identified in the solid fraction of the carbide lime slurry through X-ray powder diffraction and infrared spectrophotometry. It was also present in the liquor of the slurry, as determined by ion chromatography. Thiosulfate inhibits the oxidation of sulfite to sulfate in carbide lime liquors. Thiosulfate also interferes with Radian's iodometric sulfite determination in carbide lime, but the pH and time dependence of this interference suggests that other species are also involved.

The organic analysis of carbide lime revealed several polynuclear aromatic hydrocarbons in ppb concentrations in carbide lime. These include:

- naphthalene,
- fluorine,
- anthracene/phenanthrene,
- carbazole,
- pyrene, and
- benzo(a)pyrene.

Some of these compounds have been shown to be harmful to man and his environment. Further work is needed to determine if these compounds are leachable from carbide lime and therefore a potential threat to the environment.

Laboratory tests have confirmed that, in comparison to commercial lime slurries,

- carbide lime inhibits the oxidation of sulfite to sulfate and
- thiosulfate in a commercial lime slurry inhibits sulfite oxidation.

The exact mechanism of sulfite oxidation inhibition is unknown but the thiosulfate in carbide lime probably reacts with sulfite to form an intermediate species other than sulfate. One possible reaction, from Schroeter (Ref. 4), involves the trithionate ion ($S_3O_6^{2-}$).

$$S_2O_3^{2-} + SO_3^{2-} + 2OH\cdot(\text{radical}) + 2H^+ = S_3O_6^{2-} + 2H_2O \quad (2\text{-}1)$$

The reaction to a third, stable sulfur species (in this case, trithionate) prevents the formation of sulfate.

Antioxidants have been suggested for use in scrubbers to inhibit sulfite oxidation and thus reduce gypsum scaling potential. The amount of thiosulfate required for scale-free scrubber operation is unknown. However, to bring the thiosulfate level of commercial lime up to that found in carbide lime would cost $1.50 per ton of lime (using sodium thiosulfate pentahydrate at $12 per 100 lbs). Since commercial lime currently costs over $40 per ton (in bulk) this would represent an additional cost of less than 5 per cent. However, it is not certain that the price of thiosulfate would remain this low if a major increase in demand occurred.

The thiosulfate and reduced sulfur species in carbide lime also interfere with Radian's iodometric analytical technique. The interfering reaction is:

- time dependent. More iodine is consumed with time after the carbide lime liquor has been added.

- pH dependent. At low pH's the interference appears to decrease. However, this may be due to the increased air oxidation of iodide at low pH's thus creating a counter effect to the interference.

The bulk of the analytical interference can be attributed to the thiosulfate and reduced sulfur species in carbide lime. But the time dependence and pH dependence of the reaction suggests that other factors are involved.

The ion chromatograph was found to be the best analytical tool for determining sulfite, sulfate and thiosulfate in carbide lime liquors. The operating conditions of the ion chromatograph for analyzing each species are given in the appendix.

3.0 RECOMMENDATIONS

Further work concerning carbide lime should be concentrated in three areas, outlined below in order of commercial importance:

- the feasibility of adding sulfite oxidation inhibitors to FGD systems,
- further development of methods for analyzing sulfite, sulfate and thiosulfate in carbide lime liquors, and
- evaluation of the potential hazards of polynuclear aromatic hydrocarbons found in carbide lime on man and his environment.

If the oxidation of sulfite to sulfate could be inhibited in a FGD system, then the scrubber solution would remain subsaturated with respect to gypsum and scale would not form. Sulfite oxidation could be controlled by adding inhibitors, such as those found in carbide lime, to a wet scrubber. Therefore, it would be important to study the mechanism of sulfite oxidation in the presence of inhibitors in order to determine the following:

- the amounts of inhibitor to add to the scrubber to prevent scale formation,
- the economic feasibility of adding the inhibitor to FGD systems and

- the effect of the inhibitor on the scrubber slurry. Considered here will be the effect of the inhibitor on the particle size of the scrubber solids, on the pH of the solution, and on the overall scrubber chemistry.

Once the mechanism of inhibition has been identified, thiosulfate, or the antecedent to thiosulfate in carbide lime, should be tested as an inhibitor in a bench scale scrubber.

The development of field analytical methods for sulfur species would enhance the understanding of carbide lime FGD chemistry. A wet chemical technique for sulfite should be perfected in case an ion chromatograph is not available. Also, a method should be found to preserve sulfite in carbide lime liquors. This would prevent the sulfite from oxidizing to sulfate in going from the sampling site to the lab. A possible preservant for both wet chemical and ion chromatographic methods is formaldehyde.

Finally, several polynuclear aromatic hydrocarbons were found in carbide lime solids in ppb concentrations (see Table 5-2). These compounds may be hazardous to the environment. Therefore, the following studies are recommended:

- the leachability of these compounds in water,
- their behavior in the FGD units and
- the best method to dispose of them if they are found to be hazardous.

4.0 BACKGROUND

In this section results of a literature search conducted under this study are presented. The search covered the following areas:

- the chemical make-up of carbide lime, the conditions under which it is made and its differences from commercial lime,
- sulfite oxidation, including the various mechanisms of sulfite oxidation, known inhibitors of sulfite to sulfate oxidation and possible indirect inhibitors of sulfite oxidation,
- various aspects of sulfur chemistry, including the many oxidation states sulfur may have in aqueous solution, their reactions with sulfite, and ways in which these sulfur species may interfere in the sulfite analysis, and
- analytical methods for determining sulfite, sulfate and thiosulfate. (These methods will be presented in Section 8.0 along with descriptions of analytical methods used in this work).

4.1 Carbide Lime Characteristics

Carbide lime is a byproduct of the manufacture of acetylene. Calcium carbide and water are reacted together to

produce acetylene and carbide lime:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2 \qquad (4\text{-}1)$$

The reaction is exothermic.

The calcium carbide (CaC_2) in Reaction 4-1 is made from the reaction of calcium oxide and carbon in an electric arc furnace:

$$CaO + 3C = CaC_2 + CO \qquad (4\text{-}2)$$

Commercially, calcium carbide is most often produced by burning coke and limestone (Ref. 1). All of the nonvolatile impurities in the coke and limestone are retained in the calcium carbide. The contained impurities undergo some chemical changes due to the high temperatures and reducing conditions involved.

Carbide lime is mainly composed of calcium hydroxide and calcium carbonate. Examples of carbide lime compositions are given in Table 4-1. Along with the inorganic compounds noted, carbide lime may also contain organic compounds (Ref. 1).

Carbide lime can be used in place of commercial lime in FGD units because of its high calcium hydroxide content. The important differences between the two limes are mainly due to the higher impurities in carbide lime. Some chemical and physical differences in the two limes are given below (Ref. 1).

- There is much less magnesium and phosphorous in carbide lime than in commercial lime.

TABLE 4-1. CARBIDE LIME COMPOSITION

Compound	Weight % Source: Chemico/Mitsui (Ref. 2)	Source: Miller, S.A. (Ref. 1)
$Ca(OH)_2$	84.3	96.30
$CaCO_3$	6.9	N.R.
$CaSO_3$	1.8	N.R.
$CaSO_4$	1.0	0.34
SiO_2	1.7	1.41
Al_2O_3	0.7	1.33
Fe_2O_3	1.1	0.12
CO	N.R.	0.14
CaS	N.R.	0.08-0.12
CNS	N.R.	0.01

N.R.: Not Reported

- The amount of silicon, aluminum, carbon and iron is greater in carbide lime than in commercial lime.

- The particle size of carbide lime is less than that of commercial lime.

4.2 Sulfite Oxidation

The oxidation of sulfite (SO_3^{2-}) to sulfate (SO_4^{2-}) in aqueous solution takes place through a complex chain reaction (Ref. 3 and 4). With no catalysts or inhibitors present, the oxidation is first order with respect to sulfite.

Fuller (Ref.3) postulated that in the reaction of sulfite with oxygen, unstable intermediates are formed. Through the reduction of oxygen the following reactive radicals could be formed:

$$HO_2\cdot \qquad H_2O_2\cdot \qquad OH\cdot \qquad (4\text{-}3)$$

Also, the oxidation of sulfite could produce the following radicals:

$$SO_3^{\cdot -} \qquad S_2O_6^{\cdot =} \qquad SO_5^{\cdot -} \qquad (4\text{-}4)$$

These radicals then react to give the overall oxidation reaction:

$$SO_3^{2-} + \tfrac{1}{2}O_2 = SO_4^{2-} \qquad (4\text{-}5)$$

4.3 Inhibition of Sulfite Oxidation

The most often proposed mechanism for inhibiting sulfite oxidation is through the breaking of the chain reaction going

from sulfite to sulfate. The inhibitor species terminates the free radical chain reaction by complexing with or deactivating one of the intermediates. Schroeter (Ref. 4) states that the rate equation of the inhibition reaction is bimolecular with a first order dependence on both the radical and the inhibitor.

There has been much work done on the inhibition of sulfite oxidation (Ref. 3, 4, 5 and 6). Many organic compounds and many nitrogen compounds may be inhibitors (Ref. 4). Also, inorganic compounds such as arsenite, antimonite, phosphite and cyanide may terminate the chain reaction in sulfite to sulfate oxidation. A list of known inhibitors is presented in Table 4-2.

Another mechanism for inhibiting sulfite oxidation could be through the complexing of sulfite. Schroeter (Ref. 4) notes that pyridine possibly retards sulfite oxidation by forming the N-pyridinium sulfonic acid complex with sulfite. Not only is oxidation reduced but the end product contains significant amounts of dithionate in addition to sulfate. Formaldehyde also forms a stable complex with bisulfite, which greatly retards oxidation:

$$HSO_3^- + CH_2O = HOCH_2SO_3^- \qquad (4\text{-}6)$$

Sulfite oxidation is also inhibited if another species competes with the sulfite for oxygen. Aqueous compounds which might inhibit air oxidation of sulfite in this way are other reduced sulfur species, organic matter, and reduced inorganic compounds.

TABLE 4-2. INHIBITORS OF SULFITE OXIDATION*

methanol
ethanol
propanol
normal-, secondary-, iso- and tertiary-butyl alcohol
alkyl alcohol
ethylene glycol
glycerin
mannitol
benzyl alcohol
acetaldehyde
benzaldehyde
acetone
ethyl acetate
potassium tartrate
sodium succinate
phenol
ortho-, meta-, para-cresol
aniline
benzene

* May inhibit oxidation of sulfite when present in amounts as low as 0.00005 mole/liter.

Source: Schroeter, L. C. (Ref. 4).

4.4 Sulfur Oxide Chemistry

Through the course of this work it became apparent that there were significant concentrations of sulfur compounds in reduced oxidation states in carbide lime. These compounds are important because they may,

- inhibit sulfite to sulfate oxidation
  or
- interfere with the iodometric sulfite determination.

Therefore a brief review of pertinent sulfur chemistry is presented.

The chemistry of aqueous sulfur oxides is complex to say the least. In order to appreciate the number of reactions possible, it will help to describe some of the possible species (Ref 7):

- Sulfuric acid (H_2SO_4) is the highest oxidation state of sulfur at +6. The sulfate ion combines with calcium in scrubber liquors to form gypsum. If gypsum scale build-up is to be avoided, then sulfate formation must be inhibited.
- Thiosulfuric acid ($H_2S_2O_3$) contains sulfur atoms of oxidation states +6 and -2.

- Sulfurous acid (H_2SO_3) has a sulfur oxidation state of +4. This is the form sulfur dioxide gas takes when it is dissolved in water.

- Disulfurous acid ($H_2S_2O_5$) has sulfurs of +3 and +5 and has the chemistry of the normal sulfites.

- Dithionic acid ($H_2S_2O_6$) with a +5 sulfur is stable in aqueous solution. It is an oxidation product of bisulfite.

- Polythionic acid ($H_2S_nO_6$, where n is 3 to as much as 80) is also a stable species in water. Thiosulfate reacts with iodine below a pH of approximately 9 to form tetrathionate ($S_4O_6^{2-}$).

Many sulfur compounds may react with sulfite ion. Some of these reactions lead to a retarding of sulfite oxidation.

A mechanism which slows sulfite oxidation is the change of sulfite to another species less prone toward air oxidation. If free sulfur is present in an alkaline sulfite solution, thiosulfite is produced (Ref. 7):

$$SO_3^{2-} + S = S_2O_3^{2-} \qquad (4\text{-}7)$$

Thiosulfate is less prone toward air oxidation than is sulfite. Thiosulfate can react with sulfite to create trithionate (Ref. 4):

$$S_2O_3^{2-} + SO_3^{2-} + 2OH\cdot(\text{radical}) + 2H^+ = S_3O_6^{2-} + 2H_2O \qquad (4\text{-}8)$$

Tetrathionate ($S_4O_6^{2-}$) has also been shown to react with sulfite (Ref 8) to form trithionate:

$$S_4O_6^{2-} + SO_3^{2-} = S_3O_6^{2-} + S_2O_3^{2-} \qquad (4\text{-}9)$$

However, researchers disagree as to the stability of trithionate in solution.

Other sulfur compounds may react to create intermediates which subsequently react with sulfite. One example is:

$$S_2O_3^{2-} = S_2O_3^{-} + e^{-} \text{ and } 2S_2O_3^{-} = S_4O_6^{2-} \qquad (4\text{-}10)$$

The tetrathionate may then combine with sulfite to produce trithionate.

The above-mentioned mechanisms for the inhibition of sulfite oxidation all involve reactions with sulfur oxides in reduced oxidation states (below the oxidation state of sulfate). These same sulfur oxides, because of their reduced state, can react with iodine and interfere with the sulfite analysis (see Section 7.2). Sulfur oxides in reduced oxidation states are abundant in carbide lime and are capable of inhibiting sulfite oxidation and reacting with iodine.

5.0 CARBIDE LIME CHARACTERIZATION

Carbide lime collected at Paddy's Run was analyzed to identify possible oxidation inhibitors and analytical interferents. The concentrations of trace elements in carbide lime were determined and compared to the magnitude of the interference to help identify possible interfering species. This section reports the results of the various analyses of carbide lime and suggests possible oxidation inhibitors and analytical interferences.

There is no way to directly measure the concentration of the sulfite oxidation inhibitor without prior identification of the reponsible compound or compounds. However, if the interfering species and the inhibitor are the same, then the known concentration of the interfering species can be used as the inhibitor concentration. Preliminary work at LG&E strongly suggested that the interference with the sulfite iodometric determination was caused by a sulfur species, based on analyses and sulfur balances performed on carbide lime slurry liquors. The background work presented in this report (Section 4.4) also shows that reduced sulfur oxides can inhibit sulfite oxidation. In fact, any species in a metastable reduced oxidation state could both react with iodine and compete with sulfite for oxidation. Therefore, in this section, elements present in amounts comparable to the known analytical interferent concentration may be considered as possible oxidation inhibitors.

Later in this report, (see Section 6.3), it is shown that the concentration of the interfering species in the carbide lime slurry* liquor is on the order of 2 mmoles/liter, assuming the

*The lime slurry as it is added to the scrubber at Paddy's Run.

equivalency of the interfering species is the same as sulfite. If the interfering species does not have the same equivalency as sulfite then the molarity may be in error within an order of magnitude. Knowing the weight per cent solids in the carbide lime slurry, and assuming the dissolved species in the liquor originally came from the solids, the concentration of the interference in the solids is at least 10^{-2} mmole/gm:

$$\frac{2 \text{ mmole of interferent}}{1000 \text{ gm of liquor}} \times \frac{1000 \text{ gm of liquor}}{124 \text{ gm of solid}} \text{ (11\% solids in slurry)}$$

$$= \frac{10^{-2} \text{ mmole of interferent}}{\text{gm solid}} \qquad (5\text{-}1)$$

In this section, results of chemical analyses of both the solids and the liquors from carbide lime are reported. These analyses were conducted in light of the concept that elements present in amounts comparable to the concentration of the analytical interference were to be considered as potential oxidation inhibitors.

The solids used in the carbide lime analysis came from two sources:

- Solids filtered from the carbide lime additive slurry. The slurry contained approximately 11% by weight carbide lime solids slurried in water from the acetylene manufacturing plant.

- Solids taken from the storage piles adjacent to Paddy's Run station. These solids were taken from a settling pond in the acetylene plant and stored in piles. They were 48% solids by weight.

All analyses are based on the weight of the respective solids, dried at 45°C.

The liquor used in the analyses was filtered from the carbide lime additive. In certain analyses the solids from the storage pile were leached using deionized water. The liquor from these analyses will be referred to as carbide lime extract.

5.1 Spark Source Mass Spectrometry

The spark source mass spectrometer (SSMS) is a survey analytical instrument for determining as many as eighty elements in trace amounts. A spark source ionizes the elements in the sample. The ions are then focused into a beam electrostatically. The ions are magnetically segregated and detected according to their mass to charge ratio. The results are accurate within a factor of plus or minus two. Any element with a concentration greater than about 1000 ppm is designated as a major component (MC). Table 5-1 contains the SSMS data on the carbide lime solids from the slurry additive.

As can be seen from Table 5-1, only certain elements are of great enough concentration to cause the interference observed. At least 10^{-2} mmole/gm of the element is necessary before it can be considered as the interfering species. The following elements are of large enough concentration:

- barium, strontium, iron, manganese, titantium, calcium, potassium, chlorine, sulfur, phosphorous, aluminum, silicon, magnesium, and sodium.

TABLE 5-1. SPARK SOURCE MASS SPECTROMETER RESULTS ON SOLIDS FROM CARBIDE LIME SLURRY. SLURRY IS THE SAME AS THAT ADDED TO SCRUBBER AT PADDY'S RUN

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	4	Terbium	<0.1	Ruthenium		Vanadium	12
Thorium	2	Gadolinium	0.6	Molybdenum	11	Titanium	MC
Bismuth		Europium	0.2	Niobium	0.3	Scandium	1
Lead	4	Samarium	3	Zirconium	6	Calcium	MC
Thallium		Neodymium	2	Yttrium	4	Potassium	≥600
Mercury	NR	Praseodymium	1	Strontium	100	Chlorine	270
Gold		Cerium	13	Rubidium	0.4	Sulfur	MC
Platinum		Lanthanum	5	Bromine	≤4	Phosphorus	330
Iridium		Barium	120	Selenium	1	Silicon	MC
Osmium		Cesium	0.1	Arsenic	≤1	Aluminum	MC
Rhenium		Iodine	≤0.5	Germanium	0.5	Magnesium	MC
Tungsten		Tellurium		Gallium	5	Sodium	MC
Tantalum		Antimony	0.5	Zinc	32	Fluorine	≈43
Hafnium		Tin	0.4	Copper	13	Oxygen	NR
Lutetium		Indium	STD	Nickel	5	Nitrogen	NR
Ytterbium		Cadmium	≤0.2	Cobalt	0.9	Carbon	NR
Thulium		Silver	<0.1	Iron	MC	Boron	5
Erbium	≤0.1	Palladium		Manganese	490	Beryllium	0.3
Holmium	0.1	Rhodium		Chromium	22	Lithium	27
Dysprosium	0.3					Hydrogen	NR

NR - Not detected by SSMS

All elements not reported <0.1 ppm weight

Sample was thermally ashed @ 350°C for one hour in a laboratory furnace in a quartz crucible prior to analysis.

MC - Major Component

Several of these elements:

- aluminum, silicon, magnesium, sodium, potassium, titanium, barium, strontium, and calcium,

should be considered as nonreactive ions or insoluble silicates. Nitrogen and carbon are not detected in the SSMS data. However, they both are present in compounds which are known to inhibit sulfite oxidation (Ref 4), and therefore will be included as possible inhibitors. This makes a total of eight elements in the carbide lime solids which can be suspected as being the interfering/inhibitor species.

Table 5-2 lists the results of the SSMS analysis of carbide lime liquors. These liquors were filtered from the carbide lime additive.

The concentration of the analytical interferent at Paddy's Run FGD unit is on the order of 2 millimoles per liter of scrubber liquor. Only a few elements in the liquor are present in this large of a concentration:

- calcium,
- potassium,
- chlorine, and
- sulfur.

In addition, carbon and nitrogen are not detected by the SSMS and they may be interfering species. If the possible inter-

TABLE 5-2. SPARK SOURCE MASS SPECTROMETER RESULTS ON FILTRATE FROM CARBIDE LIME SLURRY. SLURRY IS THE SAME AS THAT ADDED TO SCRUBBER AT PADDY'S RUN.

CONCENTRATION IN µg/ml

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	0.01	Terbium		Ruthenium		Vanadium	0.006
Thorium		Gadolinium		Molybdenum	0.02	Titanium	0.005
Bismuth		Europium		Niobium	<0.001	Scandium	<0.001
Lead	0.007	Samarium		Zirconium	0.003	Calcium	MC
Thallium		Neodymium		Yttrium	≤0.003	Potassium	MC
Mercury	NR	Praseodymium		Strontium	13	Chlorine	MC
Gold		Cerium	<0.001	Rubidium	0.4	Sulfur	>3
Platinum		Lanthanum	≤0.008	Bromine	1	Phosphorus	0.5
Iridium		Barium	6	Selenium	≤0.02	Silicon	2
Osmium		Cesium	0.02	Arsenic	0.2	Aluminum	0.4
Rhenium		Iodine	0.08	Germanium	≤0.002	Magnesium	0.4
Tungsten		Tellurium		Gallium	0.01	Sodium	MC
Tantalum		Antimony	≤0.006	Zinc	0.03	Fluorine	≈6
Hafnium		Tin	0.001	Copper	0.02	Oxygen	NR
Lutetium		Indium	STD	Nickel	INT	Nitrogen	NR
Ytterbium		Cadmium	≤0.003	Cobalt	≤0.001	Carbon	NR
Thulium		Silver		Iron	0.06	Boron	0.08
Erbium		Palladium		Manganese	0.005	Beryllium	
Holmium		Rhodium		Chromium	0.05	Lithium	>1
Dysprosium						Hydrogen	NR

NR - Not detected by SSMS

All elements not reported <0.001 µg/ml

Sample was thermally ashed @ 350°C for one hour in a laboratory furnace in a quartz crucible prior to analysis.

INT-Interference

MC - Major Component

fering/inhibitor species found in the liquor are cross-checked with those possible in the solids, only four remain as candidates for the interfering/inhibitor species:

- chlorine,
- sulfur,
- carbon and
- nitrogen.

5.2 Gas Chromatography-Mass Spectrometry

The organic fraction of the carbide lime solids was analyzed on a gas chromatograph-mass spectrometer (GC-MS). The ability of many organics to inhibit sulfite oxidation is mentioned in Section 4.

The solids were filtered from the standard carbide lime additive. The organic fraction was then extracted into ethyl ether for GC-MS analysis. Radian's gas chromatograph has a six foot column with a 2.0 mm inner diameter. The packing is 1% SP 2250 on 100/120 mesh Supelcoport. The mass spectrometer is a Hewlett Packard 5980 A with glass jet separator and 70 eV power source.

The only organic materials found in the solids were several polynuclear aromatic hydrocarbons and some aliphatic hydrocarbons. The aliphatic hydrocarbons are long chain alkanes and would not affect FGD scrubber chemistry. The poly-

nuclear aromatics are listed in Table 5-3. Although these compounds are not important within the confines of this report, several are known cancer-causing agents. Therefore, it is recommended that further work be conducted to determine the concentration of these compounds in leachates of carbide lime.

The results of the GC-MS analysis on the carbide lime liquors are in Table 5-4. The aliphatic hydrocarbons found are not listed; these alkanes have carbon chains ranging around 20 carbon atoms long with concentrations in the liquor no greater than 150 ppb. They are not important in this study.

TABLE 5-4. CONCENTRATION OF MAJOR ORGANICS IN CARBIDE LIME LIQUORS AS DETECTED ON THE GAS CHROMATOGRAPH-MASS SPECTROMETER

Compound	Concentration, ppb (μg/kg)
Napthalene	8
Anthracene/Phenanthrene	2

In summary, no organic species were found on the GC-MS in either the solid or liquid portion of the carbide lime additive which could cause the analytical interference or the oxidation inhibition observed.

5.3 Sulfur Analysis

This section reports analyses of carbide lime for several different sulfur compounds. Sulfur was one of the four elements found by SSMS which is in high enough concentrations to be suspected as the interfering/inhibitor species.

TABLE 5-3. CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS AND RELATED SPECIES IN CARBIDE LIME SOLIDS

Compound	Concentration, ppb (µg/kg) A	B	C
Naphthalene	470.	450.	600.
2-Methyl naphthalene	94.	58.	73.
1-Methyl naphthalene	64.	46.	78.
Biphenyl	36.	26.	46.
C_2-Alkylnaphthalene	44.	35.	58.
C_2-Alkylnaphthalene	10.	10.	14.
C_2-Alkylnaphthalene	6.		
Acenaphthylene	84.	79.	99.
Acenaphthene	42.	22.	75.
Fluorene	108.	74.	144.
Methyl fluorene	49.	52.	104.
Anthracene/Phenanthrene	150	190.	480.
Acridine	17.		
Methylanthracene	22.	24.	76.
Carbazole	120.	134.	170.
Acephenanthrene	2.		
Fluoranthene	59	99.	240.
Pyrene	37.	54.	120.
Methylpyrene	16.		
Dimethylpyrene	3.		
Chrysene	30.	55.	140.
Benzofluoranthene	11.	38.	87.
Benzo(a)pyrene	12.	19.	35.
Indeno(c,d)pyrene	1.		
Benzo(g,h,i)perylene	2.		
Methylbiphenyl		52.	87.
Methylanthracene		26.	59.

Aliquots A, B and C are all solid samples filtered from the standard carbide lime additive. They were not dried before the extraction.

5.3.1 Sulfide

The results of the sulfide (S^{2-}) analyses on both the storage pile solids and the carbide lime additive solids showed no sulfide. An Orion Ag_2S electrode specific for sulfide ion was used for the determinations. This electrode is capable of detecting sulfide as low as 10^{-17} molar. There are no known interferences with the technique (Ref. 9).

5.3.2 Total Sulfur, Sulfate Sulfur and Pyritic Sulfur

Total sulfur, sulfate and pyritic sulfide were analyzed on one solid sample according to the standard method for "Forms of Sulfur in Coal" (Ref. 10).

The results are in Table 5-5. The total sulfur in carbide lime solids was 0.31 % by weight. There was 0.15% sulfur (or about half of the total sulfur) as sulfate and no pyritic sulfur (FeS_2). Therefore, a little over half of the total sulfur present in carbide lime is in some other form than sulfide or sulfate. This means that over half of the sulfur present in the solids is in a reduced oxidation state. This amount of reduced sulfur could create the interference with the sulfite analytical method or cause the inhibition of sulfite oxidation observed at Paddy's Run FGD unit.

TABLE 5-5. ANALYSIS OF SULFUR SPECIES IN CARBIDE LIME SOLIDS TAKEN FROM WASTE HEAP ADJACENT TO PADDY'S RUN

Dry Weight % as Sulfur (S)			
Total Sulfur	Sulfate Sulfur	Pyritic Sulfur	Other
0.31	0.15	0	0.16

5.3.3 Sulfur Species in Carbide Lime Liquors

The purpose of these analyses was to determine the amount and form of the sulfur that would leach out of the solid carbide lime. This is important if a sulfur species is the analytical interferent or oxidation inhibitor in carbide lime slurries.

Two sets of sample analyses were done. One sample came from the liquor of the carbide lime additive and one from an aqueous extraction of the solids from the storage piles. A comparison of the two shows to what extent the interfering/inhibitor species is concentrated in the acetylene process water. Acetylene process water is used to slurry the solids for the standard caribde lime additive, while the aqueous extraction was carried out using deionized water under a nitrogen atmosphere.

Table 5-6 lists the sulfur species in the liquor of the carbide lime additive and in the aqueous extract of carbide lime solids. Both of the samples were analyzed by ion chromatography. The very low concentrations of thiosulfate in carbide lime liquors prohibit the use of conventional wet chemical techniques. Radian developed a method for the analysis of thiosulfate on the ion chromatograph near the end of this study. Therefore, some of the work in this report was done before the thiosulfate procedure was developed and thiosulfate values are not available.

TABLE 5-6. SULFUR ANALYSIS ON FILTRATE FROM CARBIDE LIME ADDITIVE AND ON CARBIDE LIME SOLIDS EXTRACTED WITH WATER

	Millimoles/Liter as Sulfur (S)				
Sample	SO_4^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	S Total	Other (by difference)
Filtrate	0.017	0	1.52	2.14	0.60
Extract	0.0225	0	N. R.	0.128	0.106

N. R. - Not reported. The technique for thiosulfate was not developed at this time.

5.4 X-Ray Powder Diffraction

The carbide lime solids from the storage piles were analyzed by X-ray powder diffraction using copper radiation. Table 5-7 lists the major and minor species found. Also, some trace species are included but these are present in amounts that approach the lower detection limits of the X-ray diffractometer.

TABLE 5-7. X-RAY DIFFRACTION ANALYSIS OF CARBIDE LIME SOLIDS

Compound Name	Chemical Formula	CRYSTAL SYSTEM
---------- Major Species ----------		
Portlandite	$Ca(OH)_2$	Hexagonal
---------- Moderate Species ----------		
Calcite	$CaCO_3$	Hexagonal
---------- Minor Species ----------		
α-Quartz	SiO_2	Hexagonal
---------- Probable Trace Species ----------		
Ettringite	$\{Ca_6[Al(OH)_6]_2 \cdot 24H_2O\}$ $\{(SO_4)_3 \cdot 1\frac{1}{2}H_2O\}$	
---------- Possible Trace Species ----------		

(continued)

Lime	CaO	Cubic
Gypsum	$CaSO_4 \cdot 2H_2O$	Monoclinic
Arconite	K_2SO_4	Orthorhombic
	K_2SO_4	Hexagonal
Aphthiotolite	$(Na, K)_2SO_4$	Hexagonal
Glauber's Salt	$Na_2SO_4 \cdot 10H_2O$	Monoclinic
	$K_2Ca_2(SO_4)_3$	
Hydroxyl Ellestadite	$Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$	Hexagonal
	$CaS_2O_3 \cdot 6H_2O$	

As expected, the major component is portlandite, $Ca(OH)_2$. Calcite ($CaCO_3$) and quartz (SiO_2) are present in smaller amounts. The remaining solids are probably sulfate salts with the possibility that some thiosulfate salts are present.

5.5 Infrared Spectrophotometry

A Perkin-Elmer Model 283 infrared (IR) spectrophotometer was used to study the carbide lime solids. Thiosulfate exhibits characteristic bands at approximately 1000 and 1130 wave numbers (cm^{-1}). Figure 5-1 is the IR spectrum of reagent grade sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$.

In Figure 5-2 and 5-3 are the IR spectra of freshly dried carbide lime solids. They both have bands near 1000 and 1130 cm^{-1} similar to thiosulfate. A carbonate band is present at about 1470 cm^{-1}.

Figure 5-4 is an IR spectrum of carbide lime solids which have been dried and stored for almost a year. Note the absence of the large bands characteristic of thiosulfate. It appears that thiosulfate is present in the fresh solids but has

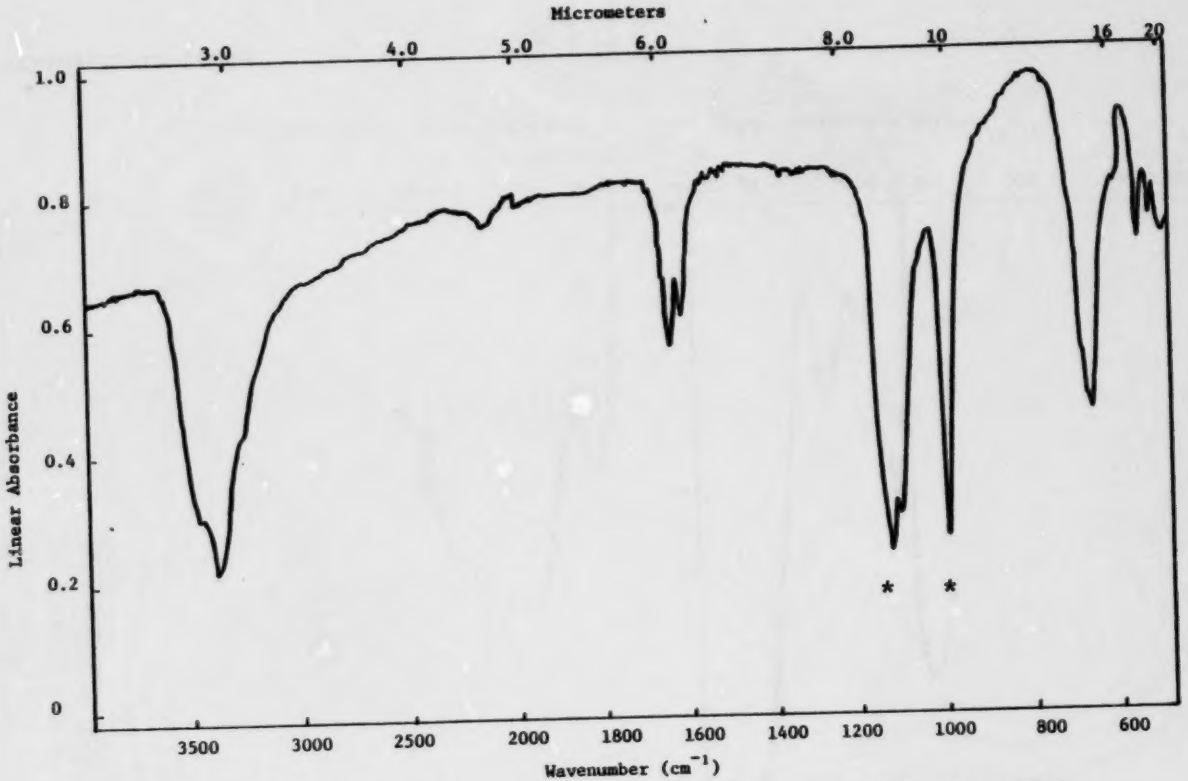

Figure 5-1. Infrared Spectrum of Reagent Grade Sodium Thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$.

*Thiosulfate bands.

02-2617-

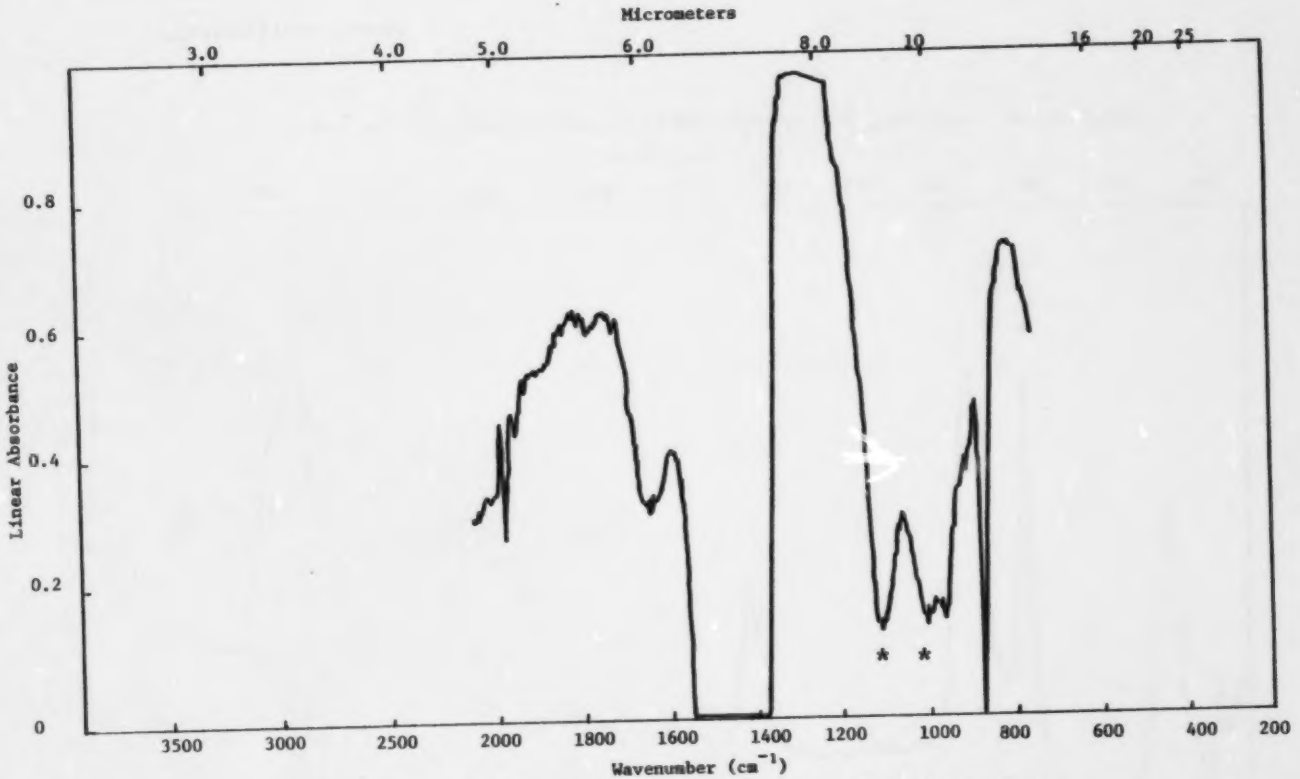

Figure 5-2. Infrared Spectrum of Freshly Dried Carbide Lime Solids.

*Thiosulfate bands.

02-261

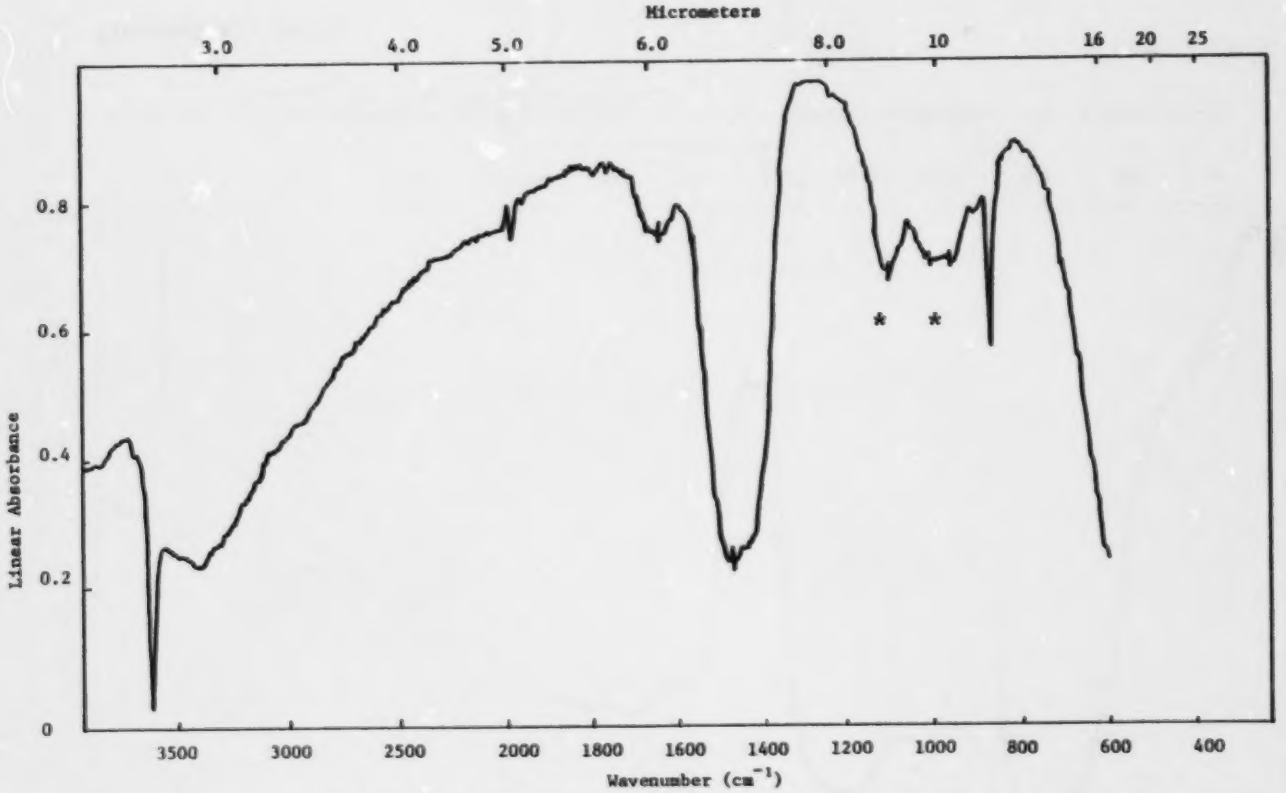

Figure 5-3. Infrared Scan of Freshly Dried Carbide Lime Solids.

*Thiosulfate bands.

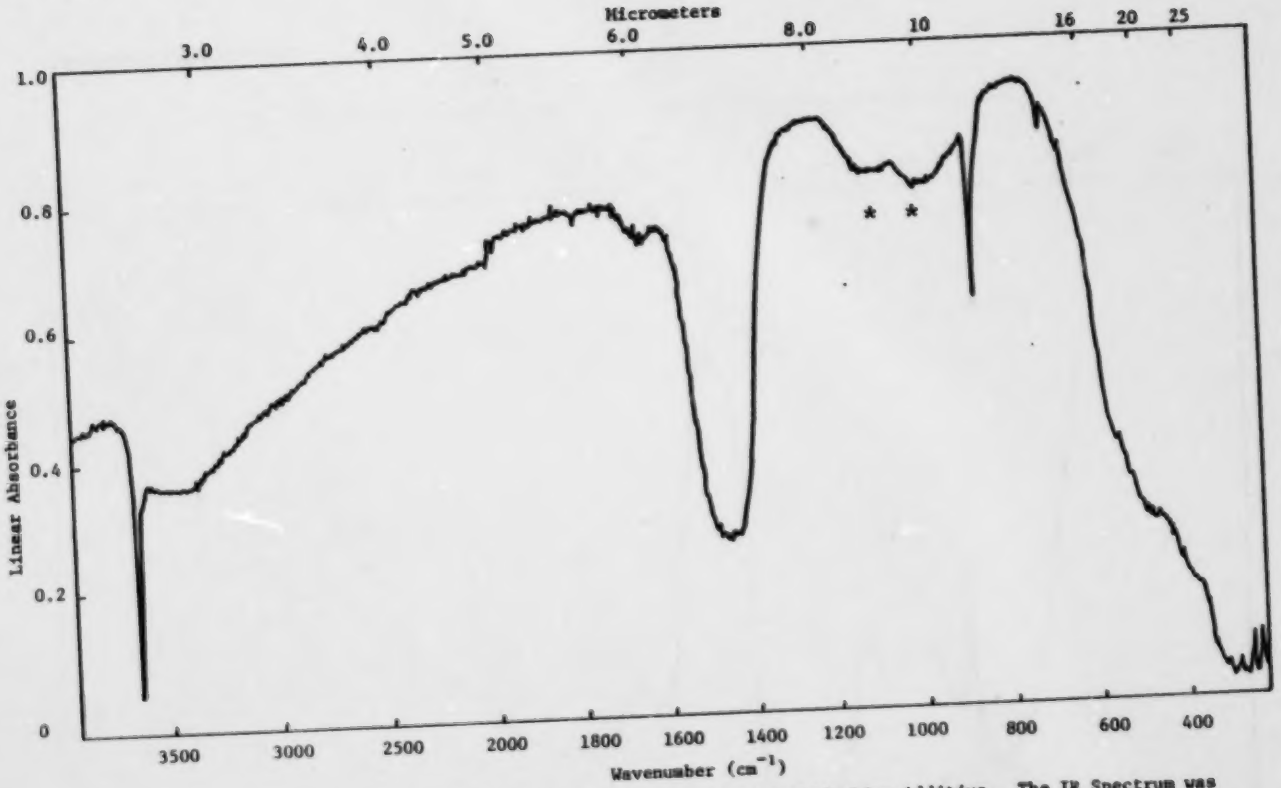

Figure 5-4. Infrared Spectrum of Dried Solids from the Standard Carbide Lime Additive. The IR Spectrum was Taken One Year After the Solids Were Dried.

*Thiosulfate bands.

02-2610-

almost disappeared in the stored solids. It is unknown why the thiosulfate is gone in the dried solid. Most likely the thiosulfate has oxidized to sulfate.

6.0 ASSESSMENT OF POSSIBLE OXIDATION INHIBITORS

One main goal of this study was to assess carbide lime as an inhibitor of sulfite oxidation. At LG&E's Paddy's Run station, no scaling was observed in the FGD unit when carbide lime was used as the scrubbing agent. Scaling was prevented because carbide lime inhibited the oxidation of sulfite to sulfate. Scaling did occur when commercial lime was used.

This section considers how carbide lime inhibits sulfite oxidation in an FGD unit. First, it will be shown that carbide lime does inhibit the oxidation of sulfite to sulfate. And second, the source and nature of the oxidation inhibitor will be discussed.

6.1 Inhibition of Sulfite Oxidation by Carbide Lime

6.1.1 LG&E Studies

No gypsum scale formed when carbide lime was used in the SO_2 scrubber at Paddy's Run station. When commercial lime was used, gypsum scaling in the scrubber occurred relatively early in the testing. The reason for the reduced scaling with carbide lime is the lowered sulfite oxidation. This is best represented numerically by the oxidation fraction, which is defined as:

$$\text{Oxidation Fraction} \equiv \frac{(\text{sulfate})}{(\text{sulfate} + \text{sulfite})}$$

where "sulfate" and "sulfite" are the fraction of calcium sulfate and calcium sulfite, respectively, found in the scrubber solids.

The oxidation fraction at Paddy's Run SO_2 scrubber was around 0.1 when carbide lime was used. This fraction increased to about 0.15 or more when commercial lime was used under the same operating conditions. This shows the reduction in sulfate formation when carbide lime is used.

6.1.2 Laboratory Studies

A test cell containing a carbide lime slurry was shown to inhibit sulfite oxidation in comparison to a similar test cell containing a commercial lime slurry. The carbide lime solids were taken from the storage piles adjacent to Paddy's Run station; the commercial lime was Austin white lime.

The lime was dissolved in boiled deionized water by the addition of 6 M HCl until a stable pH of 5 was reached. Then a weighed amount of sodium sulfite was added to the solution. The pH and major species concentrations were selected to avoid precipitation of $CaSO_3 \cdot \frac{1}{2}H_2O$. Compressed air was bubbled through the solution at a constant flow rate to oxidize the sulfite. Aliquots of the solution were taken every ten minutes and run on the ion chromatograph to measure the amount of sulfate being produced. Sulfite concentration was also monitored.

The results of these tests may be seen graphically in Figure 6-1. When using commercial lime, most of the sulfite was oxidized within ten minutes. With carbide lime, sulfite was still being produced for up to two hours. The inhibition of sulfite oxidation by carbide lime was significant.

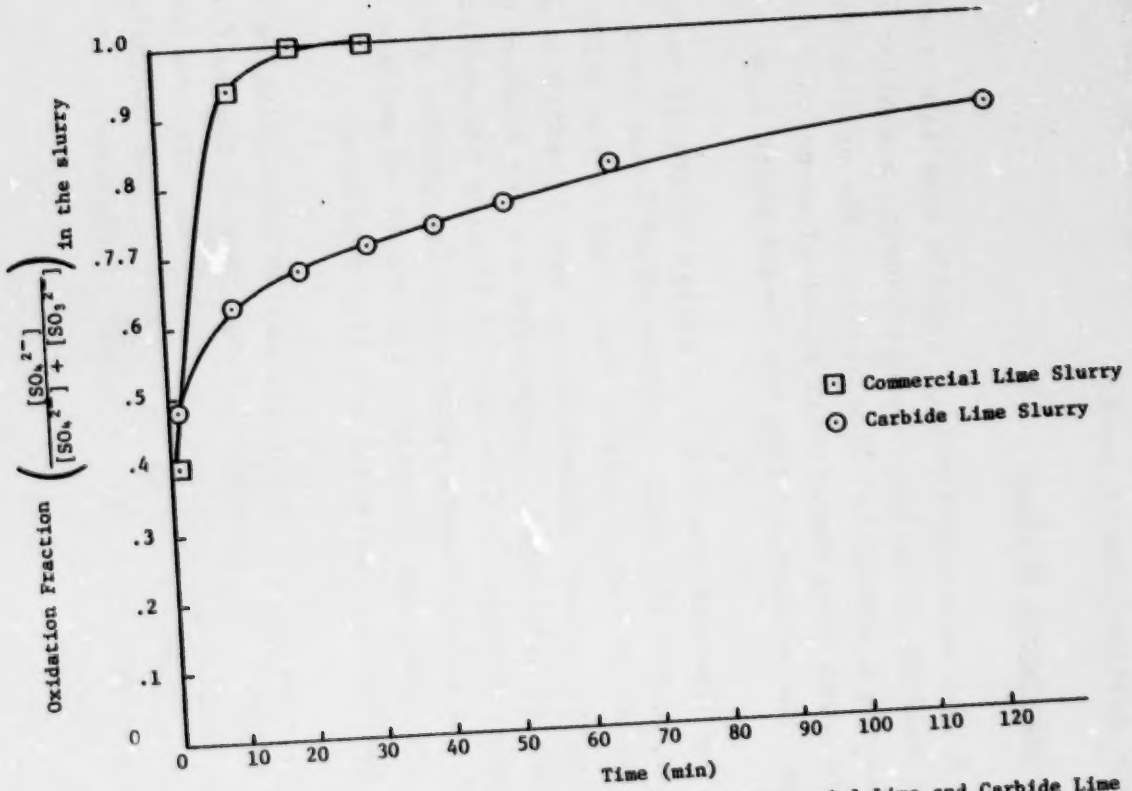

Figure 6-1. Oxidation of Sulfite to Sulfate in Commercial Lime and Carbide Lime Slurries

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The total Na_2SO_3 added initally to both lime slurries made a 2 millimolar (mmole/ℓ) solution. The carbide lime test solution initially had approximately 0.3 mmole/ℓ of sulfate and the commercial lime 0.1 mmole/ℓ . After complete sulfite oxidation, the total sulfate present in the carbide lime and commercial lime test cells should have been 2.3 mmole/ℓ and 2.1 mmole/ℓ, respectively. However, neither lime solution attained this sulfate concentration after oxidation. The carbide lime solution leveled off at about 1.4 mmole/ℓ sulfate, leaving 0.9 mmole/ℓ sulfate unaccounted for as either sulfite or sulfate. And the commercial lime solution finished at 1.7 mmole/ℓ sulfate leaving 0.4 mmole/ℓ sulfate unaccounted for.

This loss of sulfite to a species other than sulfate can be seen graphically in Figure 6-2. Here, the same data as in Figure 6-1 is plotted as a function of sulfate formation:

$$[SO_4^{2-}]/\left([SO_3^{2-}] \text{ initially added}\right)$$

If all the sulfite originally added were oxidized to sulfate, then the curves would level off at 1.0. However, both solutions, especially the carbide lime solution, seemed to have lost much of the sulfite before it oxidized to sulfate. Some explanations for this are:

- loss of sulfite as SO_2 to the air during the experiment. Since the experiments were run at a pH of 5, it is conceivable that some loss occurred. This could account for the loss in both the commercial lime and the carbide lime solution, or

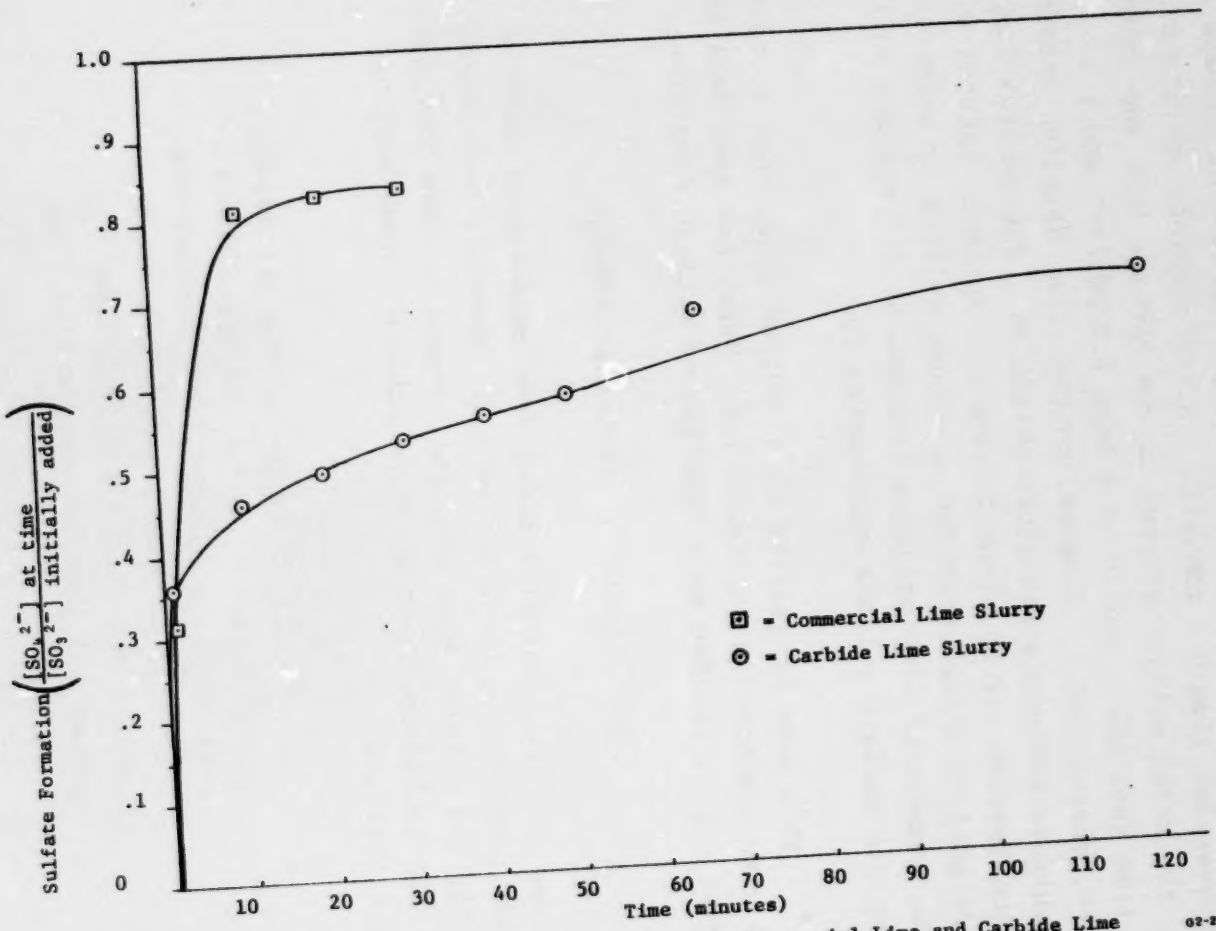

Figure 6-2. Oxidation of Sulfite to Sulfate in Commercial Lime and Carbide Lime Slurries.

- conversion of sulfite to another species besides sulfate. This is what probably occurred in the carbide lime test to account for the large amount of missing sulfate.

6.2 Possible Oxidation Inhibitors

From the analysis of carbide lime (Section 5.1) four elements were designated as possible sulfite oxidation inhibitors:

- carbon,
- nitrogen,
- sulfur and
- chlorine.

Of the four possible elements, a sulfur species is the most likely oxidation inhibitor. This is based on two facts:

- Much of the sulfur present in the carbide lime is in a reduced oxidation state (see Table 5-5 and 5-6); a reduced species could compete with sulfite for oxidation, thus limiting the amount of sulfite that is oxidized.
- Many sulfur species are known to react with sulfite (see Section 4.3). These reactions could inhibit sulfite

oxidation by changing sulfite to a species other than sulfate.

In this section the magnitude of the analytical interference will be compared to the concentrations of sulfur species. Finally, a reduced sulfur species (thiosulfate) will be assessed as a sulfite oxidation inhibitor.

6.2.1 Magnitude of Inhibitor

The magnitude of the analytical interference at LG&E's Paddy's Run scrubber was calculated by subtracting the true sulfite number from the value obtained by iodine titration at pH 6. The true sulfite number was taken as that obtained at a pH of 1. However, the number obtained at a pH of 1 may be low due to the increased air oxidation of iodine at low pH's (see Section 8). Unfortunately, these were the only sulfite values obtained at Paddy's Run.

The magnitude of the sulfite analytical interference was also determined in the laboratory at Radian. These values were obtained by comparing the pH 6 iodine titration with the "true" sulfite as analyzed on the ion chromatograph (IC). The scrubber liquor was generated on a bench scale SO_2 scrubber. SO_2 gas was bubbled through carbide lime additive in a controlled concentration and flow rate. Parameters such as pH, gas flow and solids content were monitored to simulate scrubber operating conditions at LG&E's Paddy's Run FGD unit.

Finally, the carbide lime additive liquor was analyzed on the IC for thiosulfate, sulfate and total sulfur. The total sulfur was determined by oxidizing all of the dissolved sulfur species to sulfate and then analyzing for sulfate on the IC. The amount of sulfate (SO_4^{2-}) originally present in the liquor

was subtracted from the total sulfur to obtain the "Total Non-Sulfate Sulfur". These values and those calculated for the interferent are compared in Table 6-1.

As can be seen in Table 6-1, the magnitude of the sum of thiosulfate and other reduced sulfur is the same as that of the analytical interference. This amount of reduced sulfur species would also produce the sulfite inhibition observed.

6.3 Thiosulfate as the Sulfite Oxidation Inhibitor

In this section, it will be shown that thiosulfate was verified as an inhibitor of sulfite oxidation. The exact mechanism by which thiosulfate prevents sulfite oxidation is probably through the formation of an intermediate sulfur species.

The experimental procedure for verifying thiosulfate as an oxidation inhibitor was the same as that presented in Section 6.1.2. But in this experiment the test cell contained commercial lime and sodium thiosulfate ($Na_2S_2O_3$). The lime and thiosulfate constituted a simulated carbide lime slurry. Enough sodium thiosulfate was added to make a 0.82 mM $S_2O_3^{2-}$ solution. This concentration represents an extreme case in a carbide lime slurry, where all of the reduced sulfur in the solids is dissolved as thiosulfate. Next, sodium sulfite (Na_2SO_3) was added to make a 2 mM $SO_3^{=}$ solution. This is again, the same sulfite concentration used in the previous experiment. Compressed air was bubbled through the solution at the same flow rate and aliquots were analyzed on the ion chromatograph for sulfate and sulfite.

TABLE 6-1. CONCENTRATION OF THE INTERFERENT VS THIOSULFATE AND REDUCED SULFUR IN CARBIDE LIME LIQUOR

Sulfite Analytical Interferent[1] mmole/liter as SO_3^{2-}		Standard Carbide Lime Liquor [2] mmole/liter as Sulfur		
At LG&E's Paddy's Run	From Simulated Scrubber Runs	Thiosulfate	Total Non-Sulfate Sulfur (Total Sulfur - Sulfate)	Total * Available Non-Sulfate Sulfur
2-5	3.7	1.5	2.1	4.7
	5.6			
	3.5			
	8.1			

* If all the nonsulfate sulfur available in the carbide lime solids were in solution, the concentration in standard carbide lime liquor would be 4.7 mmoles/liter. This is calculated from the sulfur analysis in carbide lime solids (Table 5-5) and the 11 weight % solids in standard carbide lime liquor.

[1] Iodometric Titration at pH 6.

[2] Analyzed by Ion Chromatography.

Figure 6-3 compares the results of this experiment with the two previous sulfite oxidation studies. It can be seen that thiosulfate significantly inhibits sulfite oxidation. In this test about half of the sulfite added initially remained unoxidized after 115 minutes. The inhibition of sulfite oxidation was much greater in this test than in the test using carbide lime slurry. Part of the reason for the greater inhibition is the large amount of thiosulfate used. The molar concentration of thiosulfate used was equivalent to the total amount of reduced sulfur found in carbide lime slurry, which seems to indicate that the other reduced sulfur species in the carbide lime do not inhibit sulfite oxidation.

Once again, the sum of the sulfite and sulfate in solution did not approach the total sodium sulfite originally added. Approximately 2 mmole/ℓ sulfite was added at time zero and at the end of 115 minutes there was 0.36 mmole/ℓ sulfate and 0.86 mmole/ℓ sulfite for a total of 1.22 mmole/ℓ. This leaves about 0.8 mmole/ℓ of the original sulfite in a form different than sulfite or sulfate. It is conceivable that some sulfite was lost to the atmosphere but not this large an amount. The thiosulfate apparently reacts with the sulfite to form another sulfur species, thus preventing the formation of sulfate ion.

6.4 Oxidation Inhibiting Reactions

Several reactions may take place between thiosulfate and sulfite to inhibit sulfite oxidation. Schroeter (Ref 4) suggests that thiosulfate and sulfite in solution produce trithionate:

$$S_2O_3^{2-} + SO_3^{2-} + 2OH\cdot(\text{radical}) + 2H^+ = S_3O_6^{2-} + 2H_2O \qquad (6\text{-}1)$$

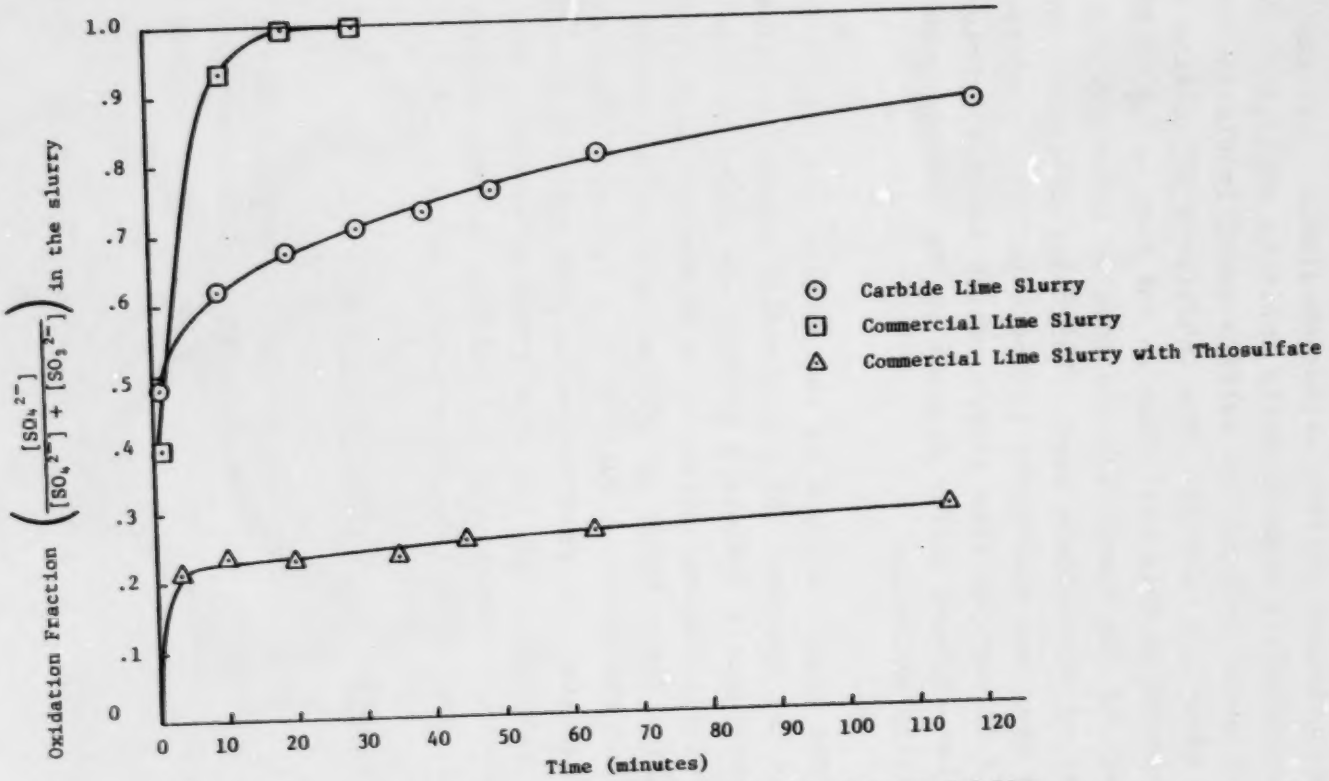

Figure 6-3. Oxidation of Sulfite to Sulfate in Slurries of Commercial Lime with Thiosulfate, Commercial Lime and Carbide Lime.

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Or, if thiosulfate were oxidized to tetrathionate ($S_4O_6^{2-}$) the following reaction could occur (Ref. 8).

$$S_4O_6^{2-} + SO_3^{2-} = S_3O_6^{2-} + S_2O_3^{2-} \qquad (6\text{-}2)$$

Reactions such as these would effectively inhibit sulfite oxidation by making sulfite unavailable for reaction. An important aspect of these reactions would be the stability of the product species (such as trithionate) toward oxidation.

Another possible mechanism of sulfite oxidation inhibition would be the oxidation of thiosulfate. Thiosulfate is a reduced sulfur species and can be oxidized to sulfate. Thiosulfate would therefore compete with sulfite for oxidation, thus lowering the amount of sulfite which is oxidized. The other reduced sulfur species present in the liquors could also compete for oxidation.

From the oxidation studies in Section 6.1.2 and 6.3, it appears that the mechanism of inhibition in thiosulfate solutions is most similar to reactions such as 6-1 and 6-2. These reactions would account for both the inhibited sulfite oxidation and for the loss of sulfite to some species other than sulfate. A competing oxidation reaction would not account for the loss of sulfite.

7.0 EVALUATION OF POTENTIAL INTERFERENCE-FREE ANALYTICAL METHODS FOR SULFITE, SULFATE AND THIOSULFATE

Knowing the concentration of sulfur species in FGD liquors is important in understanding the overall chemistry of the system. In carbide lime liquors the sulfur chemistry is complicated by the presence of thiosulfate and other sulfur species in reduced oxidation states. These other species cause interferences with normal sulfite analysis. Therefore, several methods for analyzing sulfite, sulfate and thiosulfate in carbide lime liquors were tested. The analytical method chosen for each species must be reproducible, reliable at low concentrations (millimolar) and free from interferences.

Two different sample sets were used to test the methods. One set came from the filtrate of the carbide lime additive slurry. The other set was simulated scrubber liquor, generated on a bench scale SO_2 scrubber. After each test run the liquors were analyzed for sulfur species using various trial methods.

7.1 Ion Chromatography

Ion chromatography was found to be the most reliable method for the analysis of sulfite, sulfate and thiosulfate in carbide lime liquors. Because of this, the ion chromatograph (IC) was used as the referee for other methods that were tested. Section 8 contains a brief description of the IC.

The advantage the IC offers over other analytical techniques is that the concentration of the ion of interest is

determined directly. Concentration is not measured through reaction as, for example, in the iodine titration where other species can react to give false results.

The main disadvantage with the IC concerns logistics. First, the instrument is bulky and it may not always be possible to have one on sampling trips. Second, with carbide lime liquors, the sulfite may oxidize to sulfate in transporting it from the sampling site to the IC. The latter problem could be solved, however, if the sample was preserved.

To preserve a carbide lime FGD sample, the sulfite must be prevented from oxidizing to sulfate. Several techniques are available for preventing sulfite oxidation in carbide lime liquors:

- The sample is added to a 60% isopropanol solution. This worked well in preventing sulfite oxidation in synthetic solutions. However, when carbide lime liquors generated from the simulated scrubber were preserved in 60% isopropanol some precipitation occurred. Some species that were water soluble were not soluble in isopropanol solutions.

- Another sulfite oxidation inhibitor is a 5% glycerol solution. In this case no precipitation occurred when scrubber liquors were preserved in the glycerol solution.

- Finally, a promising preservant which was not used in this study is a formaldehyde solution. Only enough formaldehyde need be present to complex all of the sulfite. The complex formed would resist air oxidation. Furthermore, the complex might prevent reaction of sulfite with interfering species in solution. Once the sample is injected into the IC, the complex breaks down on the ion exchange column and sulfite is eluted off. Further work is needed to test this on carbide lime liquors.

The instrument operating conditions for determining sulfite, sulfate and thiosulfate on the IC are in the Appendix.

7.2 Iodometric Analysis

The existence of the interfering/inhibitor species was first discovered while doing iodometric sulfite analyses of carbide lime liquors at Paddy's Run FGD unit. Both the interfering species and sulfite act as reducing agents. Therefore, an iodometric titration at pH 6 to determine the sulfite concentration resulted in a measured concentration that was too large; the iodine was consumed by both the sulfite and the interferent. Also, the reaction of the interfering species with the iodine was time dependent, that is the reaction of the interferent with iodine was relatively slow so that the longer the time before back-titration, the larger the measured concentration of "sulfite".

7.2.1 Iodometric Titration as a Function of pH

When the iodine titration was carried out at a pH of 1 there seemed to be less interference. The rate of the interfering reaction seemed to decrease from pH 6 down to pH 1. However, at low pH's a competing reaction is the oxidation of iodide to iodine by molecular O_2:

$$6I^- + O_2 + 4H^+ = 2I_3^- + 2H_2O \qquad (7\text{-}1)$$

where I_3^- is a complex formed between I_2 and I^- to solubilize the I_2. Reaction (7-1) produces iodine and the interfering reaction consumes iodine. Therefore, the two occurring together would result in an apparent decrease in the interference.

The following experiment was performed to test the reliability of the iodometric titration at low pH's in carbide lime liquors. The carbide lime additive liquor was titrated iodometrically at a pH of 1. According to ion chromatography, there should be no sulfite present in these liquors. The results of each of four runs showed that iodine was actually produced in the carbide lime liquors. This means that the air oxidation of I^- to I_2 was catalyzed by the low pH liquors. Therefore, if sulfite were present in the low pH liquors, several reactions could take place during an iodine titration:

- the I^- could be air oxidized to I_2,
- the I_2 could be reduced to I^- by sulfite,
- the interfering species also reduces I_2, and

- any number of side reactions involving sulfite and the interferent could take place.

7.2.2 Errors With the Back-Titration

The iodometric titration involves two steps (see Section 8):

- the reaction of the sample with an excess of iodine and
- the titration of the unreacted iodine with a thiosulfate standard.

The interference with the analysis could occur in either step. A back-titration using standard arsenious oxide instead of thiosulfate was done to determine if the interference is in the back-titration.

Arsenious oxide quantitatively reduces iodine between pH 7 and 9:

$$HAsO_2 + I_3^- + 2H_2O = H_3AsO_4 + 3I^- + 2H^+ \qquad (7\text{-}2)$$

Samples of both the standard carbide lime additive and the simulated scrubber liquor were added to an excess of standard iodine and back-titrated. Thiosulfate and arsenious oxide were used as back-titrants for comparison.

Different results were obtained with each back-titrant, as seen in Table 7-1. Both back-titrations show the affect of the interfering species. The "apparent" sulfite determined by

both titrations is greater than the true sulfite as determined by ion chromatography. However, the extent of the interference is different for the two titrations. More work would be needed to explain the difference between the two back-titrations.

TABLE 7-1. EVALUATION OF THE BACK-TITRATION IN THE IODOMETRIC DETERMINATION OF SULFITE IN CARBIDE LIME LIQUORS

Sample	Back-Titrant	Apparent Sulfite (mmole/ℓ)
Standard Carbide Lime Liquor	Sodium Thiosulfate	0.20
Standard Carbide Lime Liquor	Arsenious Oxide	0.63
Simulated Scrubber Liquor	Sodium Thiosulfate	3.28
Simulated Scrubber Liquor	Arsenious Oxide	5.55

True sulfite as determined on the ion chromatograph:

Simulated Scrubber Liquor - 0.72 mM
Standard Carbide Lime Liquor - 0 mM

7.2.3 Catalytic Effects

If the interfering species in the iodometric analysis of sulfite acts as a catalyst then it would not be consumed by the iodine titration. This would mean that only small amounts of interfering species are needed to cause the errors found.

Experimental results show that the interferences with the iodometric determinations are not catalytic. A 50.0 ml aliquot of standard carbide lime liquor was added to an excess of 0.100 N iodine in a pH 6 buffer. The unreacted iodine was back-titrated with 0.100 N $Na_2S_2O_3$ to a clear end point. The

liquor aliquot consumed 13.5 micromoles of iodine. Next, an additional 5.0 mls of iodine was added to the solution. If the reaction to consume iodine was catalytic then more iodine should react. However, no iodine reacted. Therefore, the interferent in the carbide lime liquor is consumed by reaction with iodine.

7.2.4 Isolating the Sulfite from the Interfering Species by Purging off Sulfur Dioxide

One method for determining the sulfite concentration in carbide lime liquors is to physically separate the sulfite and the interferent. The sulfite may then be analyzed iodometrically with no interference. This may be done by adding the sulfite sample to dilute hydrochloric acid. Sulfur dioxide gas is formed,

$$SO_3^{2-} + 2H^+ = H_2SO_3(aq) = SO_2(g) + H_2O \qquad (7\text{-}3)$$

and is purged off with an inert gas. The purged SO_2 is then trapped in a 0.1 M $NaHCO_3$ solution. The interferent should remain in the acid impinger and sulfite is determined in the $NaHCO_3$ trap.

Scrubber liquors from three simulated scrubber runs were analyzed for sulfite by this purge and trap method. The results are inconsistant. In some instances, it appears that the method may be suitable for sulfite analysis of carbide lime scrubber liquor. However, overall it appeared that the interferent might also be purged and trapped along with the sulfite. Futher work will be needed to exactly assess the value of this method, although it appears to be of little value for carbide lime liquors.

7.2.5 Isolation of Sulfite from the Interfering Species by Complexing Sulfite with Formaldehyde

When complexed with formaldehyde, sulfite is inert to iodine oxidation (see Section 4). A concentrated formaldehyde solution was required to prevent the reaction of sulfite with iodine. Concentrated formaldehyde reagent is 37% formaldehyde by weight. The pH of the formaldehyde reagent is approximately 6.

In this method the sulfite is isolated from the interfering species by complexing with formaldehyde. The sample is added to the 37% formaldehyde solution and titrated iodometrically. This titration yields the equivalents of the interfering species. A second titration is carried out on the sample in a pH 6 buffer without adding formaldehyde. This titration yields the equivalents of the sulfite plus interfering species. The equivalents of interfering species is then subtracted from the equivalents of sulfite plus interfering species. This gives the net sulfite concentration.

The results of the formaldehyde-iodometric titration are compared to the sulfite obtained by ion chromatography in Table 7-2. The test samples were generated on a bench scale SO_2 scrubber using standard carbide lime additive. The sulfite concentrations determined by the formaldehyde-iodine method are within a factor of two of the true sulfite measured by ion chromatography. This error is probably due to the slow reaction of the interfering species with iodine.

This is the most reliable wet chemical technique for sulfite analysis in carbide lime liquors. Further work is needed to prevent the time dependent reaction of the interfering species with iodine.

TABLE 7-2. COMPARISON OF SULFITE VALUE OBTAINED BY FORMALDEHYDE-IODOMETRIC TITRATION WITH ION CHROMATOGRAPHY

Sample	Ion Chromatograph (mM)			Formaldehyde-Iodometric Titration (mM)
	SO_3^{2-}	SO_4^{2-}	Total Sulfur	SO_3^{2-}
Simulated Scrubber Liquor, Run #2	1.0	6.0	10.4	1.9
Simulated Scrubber Liquor, Run #3	0.72	3.7	4.4	1.8

The formaldehyde-iodine method could also be used to determine thiosulfate in carbide lime liquors. One iodine titration of the sample is done with formaldehyde present to give the thiosulfate concentration. The next titration without formaldehyde will give the concentration of thiosulfate plus sulfite. The difference of the two titrations will yield both sulfite and thiosulfate concentrations. However, the time dependence of the iodine titration in carbide lime liquors would again create errors.

7.3 Potentiometric

This section describes a method of analyzing sulfite potentiometrically. The method involves measuring the current peaks observed when linear voltage sweeps are applied to a stationary platinum wire electrode. The electrodes are immersed in an unstirred pH 6 buffer solution containing the sulfite sample. An anodic potential sweep is used to determine sulfite.

This method is relatively free from interference since each current peak is obtained over a limited potential. In carbide lime liquors generated from the simulated scrubber both the sulfite and an unknown peak were observed. However, the instrument proved too insensitive for the measurement of both peaks. The peak for sulfite overlapped the unknown peak.

The technique was also too insensitive for identifying the interferent. Several candidates for the interfering species were spiked into carbide lime liquors and then run on the potentiostat. It was impossible to judge if their oxidation potentials matched that of the unknown peak.

7.4 Acidimetric Analysis of Sulfate

Radian has used an acid-base titration to determine sulfate in scrubber liquors. First the sample is purged of sulfite by acidifying with HCl and driving off the SO_2 formed with an inert gas. The sample is then passed through a cation exchange column in the hydrogen form. In the column the cations in the sample are exchanged for protons (H^+), forming H_2SO_4. Next, the sample is evaporated to dryness at 75°C leaving only nonvolatile acids. In scrubber liquors only sulfuric acid remains with possibly small amounts of phosphoric acid. Sulfuric acid is then determined by titrating with 0.05 N sodium hydroxide. Any phosphates present must be analyzed separately.

This method was used successfully on carbide lime scrubber liquors at LG&E's Paddy's Run station. In order to prevent oxidation of sulfite to sulfate the sample could be acidified immediately upon collection, thus driving the sulfite off as SO_2 gas.

8.0 ANALYTICAL METHODS FOR SULFITE, SULFATE, AND THIOSULFATE

It is important to know the sulfite and sulfate concentrations in FGD liquors. The degree to which sulfite oxidizes to sulfate influences when scaling occurs. Thiosulfate is important because of the significant amounts found in carbide lime and its ability to retard sulfite oxidation.

8.1 Sulfite Analysis

8.1.1 Iodometric

The standard method for sulfite analysis is an iodine titration. The iodine titrant is made by solubilizing iodine with potassium iodide, KI, to form the tri-iodide ion, I_3^-. Normally, the sulfite sample is added to an excess of iodine:

$$H_2SO_3 + I_3^- + H_2O = SO_4^{2-} + 3I^- + 4H^+ \qquad (8\text{-}1)$$

and then the excess iodine is back-titrated with thiosulfate,

$$I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-} \qquad (8\text{-}2)$$

The amount of iodine which originally was consumed by the sulfite is found by difference and is used to calculate the sulfite concentration in the sample (Ref 9).

The iodine titration is usually carried out between a pH of 1 and 8. Very low pH's promote the oxidation of iodide by the air. And in mildly alkaline solutions triiodide may disproportionate:

$$I_3^- + OH^- = 2I^- + HOI. \qquad (8\text{-}3)$$

It is, therefore, best to avoid either very acidic or alkaline solutions during an iodine titration. Radian uses a pH 6 buffer for iodine titrations.

The iodine titration may be changed to fit different sample conditions. It may be done as a direct titration with the sample being the titrant. This would minimize side reactions which take place between an excess of iodine and the sample. Secondly, in the back-titration arsenious oxide ($HAsO_2$) may be used instead of thiosulfate if there are harmful side reactions with thiosulfate.

The major problem with sulfite determination by iodine titration is the numerous species which may interfere. Other sulfur species, such as thiosulfate, sulfide, and polysulfides may also react with iodine. Many organic compounds are oxidized by iodine. Also, metal cations can act as catalysts for the reduction of iodine.

8.1.2 Ion Chromatography

Ion chromatography is a relatively new technique for measuring ions in solution. Ion exchange columns are used to separate the ions of interest which are then detected on a conductivity meter. The concentrations of the ions are determined by comparison with standard solutions. This instrument has been used by Radian to detect sulfite and sulfate in FGD liquors. Stevens and Turkelson (Ref. 11) used the ion chromatograph to measure chloride, phosphate, sulfite and sulfate in boiler blowdown waters. They were able to achieve complete separation of all the anions mentioned.

Care must be taken in making the sulfite standards because sulfite is easily oxidized to sulfate. One method is to make the standard by dissolving sodium sulfite in an oxidation inhibitor. Some suitable inhibiting solutions are:

- 60% isopropanol,
- 5% glycerol or
- formaldehyde (the amount has not yet been determined).

These solutions will prevent the sulfite standard from oxidizing. A second method for making a sulfite standard is to dissolve the sodium sulfite in deionized water. The sulfate which subsequently forms from sulfite oxidation can be measured on the IC. This sulfate value is then subtracted from the sodium sulfite initially added to obtain the concentration of sulfite in the standard.

8.1.3 Gravimetric Analysis

Sulfite can be oxidized to sulfate using any number of oxidizing agents. The sulfate formed is then precipitated as the barium salt and determined gravimetrically.

8.1.4 Other Oxidizing Titrations

Blasius et al. (Ref. 7) mentions several other titrants of sulfite. They are all oxidizing agents. Among them are bromine, permanganate, and hydrogen peroxide.

8.1.5 Complexiметric

The titration of a sulfite solution with mercuric chloride forms the complex $[Hg(SO_3)_2]^{2-}$. The complexation reaction causes a potential difference in a platinum wire coated with mercury (Ref.7).

8.2 Sulfate Analysis

8.2.1 Ion Chromatography

The use of the ion chromatograph for sulfate analysis is well documented (Ref. 11). There is no problem in making a stable standard.

8.2.2 Gravimetric

Sulfate is precipitated with $BaCl_2$ in an acidic medium. The solution is digested by heating for several minutes to minimize coprecipitation of other barium salts. The sulfate is determined gravimetrically as $BaSO_4$ (Ref. 7).

8.2.3 Colorimetric

Bertolacini and Barney (Ref. 12)have used barium chloranilate to detect sulfate. The barium chloranilate is added to a sulfate solution causing the precipitation of barium sulfate. The highly colored acid-chloranilate ion is then detected colorimetrically. The reaction is carried out at a pH of 4 and the absorption is measured at 530 mμ.

8.2.4 Complexiметric

The complexiметric determination of sulfate involves titrating the solution with either Pb^{2+} or Ba^{2+} to form an insoluble salt. The sample is added to an excess of lead or barium and the remaining cation is back-titrated with EDTA. The end point is detected using Eriochrome-black T (Ref. 7).

8.3 Thiosulfite Analysis

8.3.1 Ion Chromatography

There is no method in the literature for analyzing thiosulfate by ion chromatography. However, thiosulfate does have a definite retention time on the ion chromatograph and the use of this instrument for thiosulfate determination could greatly eliminate the interferences found in wet chemical methods. Radian is currently optimizing a method for thiosulfate analysis by ion chromatography.

8.3.2 Gravimetric

Thiosulfate can be converted to sulfate using a suitable oxidizing agent such as H_2O_2, Br_2, or Na_2O_2. The sulfate produced is then determined gravimetrically using $BaCl_2$ as the precipitant (Ref. 7).

8.3.3 Iodometric

Iodine may be used in a direct titration of thiosulfate. Thiosulfate reacts with iodine between pH's of 4.5 and 9.5 to form tetrathionate ($S_4O_6^{2-}$). At more alkaline pH's the reaction goes to sulfate non-stoichiometrically. Therefore, it is necessary to carry out the reaction below a pH of 9.5 (Ref. 7).

8.3.4 Complexiometric

The complexiometric analysis of thiosulfate involves titrating a sample with $HgCl_2$. The complex HgS_2O_3 is formed and the end point is determined potentiometrically or by the dead stop method (Ref. 7).

8.4 Mixtures of Two or More Sulfur Species

8.4.1 Sulfate-Sulfite Analysis

Sulfate and sulfite may be determined in the same solution by ion chromatography. Under the right operating conditions sufficient separation between the two species is obtainable. Also, sulfite may be analyzed iodometrically in the presence of sulfate with no interference. Sulfate may be determined gravimetrically or on the ion chromatograph.

Care must be taken to prevent sulfite from oxidizing to sulfate. Radian has developed a technique where sulfite is separated from sulfate and then both can be analyzed separately. The sample is added to 0.4 M HCl and purged with an inert gas. The sulfite decomposes to form SO_2 gas which is then expelled and trapped in an impinger containing a bicarbonate solution. The sulfite trapped in the bicarbonate is measured iodometrically. The sulfate in the original solution is analyzed on the ion chromatograph or determined gravimetrically.

8.4.2 Sulfite-Thiosulfate Analysis

The most often cited method for sulfite and thiosulfate analysis is the formaldehyde method (Ref. 7 and 8). Formaldehyde and sulfite in solution form the stable complex hydroxymethanesulfinate ($HOCH_2SO_3^-$). This complex is inert to iodine

oxidation. Formaldehyde can be added to a solution containing both sulfite and thiosulfite. The thiosulfate can then be determined iodometrically without sulfite interference. A second aliquot can be titrated with iodine without the addition of formaldehyde. The value of the second titration minus that of the formaldehyde titration gives the sulfite concentration by difference.

8.4.3 Analysis of Several Sulfur Oxides Together

The ion chromatograph could be a powerful analytical tool for sulfur species analysis in complex solutions. Radian is working on techniques for the simultaneous analysis of several sulfur oxides. Now there are few reliable wet chemical techniques for complicated sulfur solutions, especially when the concentrations are millimolar or less.

Several methods of analysis for solutions containing two or more of sulfate, sulfite, thiosulfate, sulfide and polythionate are listed by Blasius, E. et al. (Ref. 7). Most of these are variations on the wet chemical methods already mentioned in this report.

One final method specific for thiosulfate in the presence of other sulfur oxides merits attention. Danehy and Zubritsky (Ref. 8) use formaldehyde and Na_2SO_3 to determine thiosulfate iodometrically in the presence of dithionite and bisulfite. This method is of interest because it is specific for thiosulfate. The method requires at least millimolar concentrations of thiosulfate to be reliable.

REFERENCES

1. Miller, S. A., Acetylene, Its Properties, Manufacture and Uses, Vol. L. NY, Academic, 1965.

2. Environmental Protection Agency, Flue Gas Desulfurization Symposium, 1973, Proceedings, EPA 650/2-73-038. Research Triangle Park, N. C., 1973.

3. Fuller, E. C. and R. H. Crist, "The Rate of Oxidation of Sulfite Ions by Oxygen:, JACS 63, 1644 (1941).

4. Schroeter, L. C., Sulfur Dioxide. Elmsford, N.Y. Permagon, 1966.

5. Altwicker, E. R., "Sulfur Dioxide Absorption, Oxidation, and Oxidation-Inhibition", DECHEMA-Monogr. 80 (1939-1669), 343-64 (1976).

6. Kawamoto, Kensuke, et al., "Antioxidant for the Aqueous Solutions of Sulfite and/or Bisulfite of Sodium or Potassium and Process for Preventing the Oxidation of Said Aqueous Solution", U. S. Patent 3,88,969 (June 1975).

7. Nickless, G., ed., Inorganic Sulfur Chemistry, N.Y., Elsevier, 1968.

8. Danehy, James P. and Charles William Zubritsky, III, "Iodometric Method for the Deterination of Dithionite, Bisulfite, and Thiosulfate in the Presence of Each Other and Its Use in Following the Decomposition of Aqueous Solutions of Sodium Dithionite", Anal. Chem. 46(3), 391 (1974).

REFERENCES (continued)

9. Peters, Dennis G., John M. Hayes, and Gary M. Hieftje, Chemical Separations and Measurements. Philadelphia, W. B. Saunders Co., 1974.

10. American Society for Testing and Materials, 1977 Annual Book of ASTM Standards, Part 31, Water. Philadelphia, PA, 1977.

11. Stevens, Rimoty S. and Virgil T. Turkelson, "Determinations of Anions in Boiler Blow-Down Water with Ion Chromatography," Anal. Chem. 49 (8), 1176 (1977).

12. Bertolacini, R. J. and J. E. Barney, "Colorimetric Determination of Sulfate with Barium Chloranilate," Anal. Chem. 29, 281-83 (1957).

APPENDIX

STANDARD OPERATING CONDITIONS FOR THE DETERMINATION OF SULFITE, SULFATE AND THIOSULFATE CONCENTRATIONS IN CARBIDE LIME LIQUORS USING THE ION CHROMATOGRAPH

APPENDIX

Radian has applied ion chromatography to the analysis of carbide lime flue gas desulfurization solutions. Ion chromatography has been used to measure sulfite and sulfate. And recently, a method has been developed for the analysis of thiosulfate. The operating conditions for each ion are presented.

The Dionex Model 14 Ion Chromatograph uses ion exchange columns to separate individual ions, a patented suppressor column and a conductivity cell for the detection of the separated ions. The instrument can be used for the determination of either cations or anions.

Sulfite (SO_3^{2-}) and Sulfate (SO_4^{2-})

Both sulfite and sulfate are determined in one injection on the ion chromatograph. Care must be taken to prevent sulfite from oxidizing to sulfate in the sample prior to injecting into the ion chromatograph. This was done by storing the sample in either 60% isopropanol solution or 5% glycerol solution. The chromatographic conditions are shown in the table.

Thiosulfate ($S_2O_3^{2-}$)

The technique for determining thiosulfate on the ion chromatograph is relatively new. It was used for one sample in this report and the results are accurate. More work is needed to optimize the method for all conditions. Perhaps sulfite, sulfate and thiosulfate can all be determined in one injection.

TABLE A-1. CHROMATOGRAPHIC CONDITIONS

	SO_3^{2-} and SO_4^{2-}	$S_2O_3^{2-}$
Eluent	0.003 M Na_2CO_3 0.0024 M $NaHCO_3$	0.009 M Na_2CO_3 0.0072 M $NaHCO_3$
Pump Pressure	400 psi	150 psi
Analytical Column	Dionex Corp. Anion Exchanger 500 mm	Dionex Corp. Anion Exchanger 150 mm
Detector Sensitivity	30 µmhos	30 µmhos
Injector Volume	100 µL	100 µL

Standard Solutions

- Sulfate standards were made from diluted sulfuric acid.
- Sulfite standards were made by dissolving reagent grade Na_2SO_3 in a 60% isopropanol solution. Any sulfate formed was measured on the ion chromatograph and subtracted from the original sulfite.
- Thiosulfate was made by dissolving reagent grade $N_2S_2O_3$ in water. Thiosulfate is stable toward air oxidation.